

AD A 048074

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Contract N00014-76-C-0577

Task No. NR 053-612

TECHNICAL REPORT NO. 77-01

TR-77-01

Trifluoromethylsulfur Trifluoride. An Improved  
Synthesis, New NMR Data and Stereochemistry.

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Prepared for Publication

in

Journal of Inorganic Chemistry

Department of Chemistry  
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Austin, Texas 78712

21 Dec 1977

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11 p.

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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) Trifluoromethylsulfur Trifluoride. An Improved Synthesis, New NMR Data and Stereochemistry		5. TYPE OF REPORT & PERIOD COVERED Technical Report, 1977
7. AUTHOR(s) R. W. Braun, A. H. Cowley,* M. C. Cushner, and R. J. Lagow*		6. PERFORMING ORG. REPORT NUMBER TR-77 01
9. PERFORMING ORGANIZATION NAME AND ADDRESS Department of Chemistry, The University of Texas at Austin, Austin, Texas 78712		8. CONTRACT OR GRANT NUMBER(s) N00014-76-C-0577 NEW
11. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research Department of the Navy		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		12. REPORT DATE December 21, 1977
		13. NUMBER OF PAGES 9
		15. SECURITY CLASS. (of this report)
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report)		
<div style="border: 1px solid black; padding: 5px; width: fit-content; margin: 10px auto;"> <p>1. DISTRIBUTION STATEMENT - A</p> <p>Approved for public release.</p> <p>Distribution Unlimited</p> </div>		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20; if different from Report)		
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number)		
<p>Sulfur (IV) fluorides. Synthesis by direct fluorination.  <sup>19</sup>F and <sup>13</sup>C NMR data. Stereochemistry.</p> <p style="text-align: center;">C13                      F19</p>		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number)		
<p>An improved synthesis of CF<sub>3</sub>SF<sub>3</sub> has been devised which involves the direct fluorination of CF<sub>3</sub>SSCF<sub>3</sub> in a continuous flow reactor. <sup>13</sup>C and variable temperature <sup>19</sup>F NMR data have been acquired for CF<sub>3</sub>SF<sub>3</sub>. These data indicate that the CF<sub>3</sub> group occupies an equatorial site on an idealized trigonal bipyramidal structure. The barrier to intramolecular fluorine exchange in CF<sub>3</sub>SF<sub>3</sub> is unusually high ( &gt; 17 kcal/mole).</p>		

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Trifluoromethylsulfur Trifluoride. An Improved Synthesis,  
New NMR Data and Stereochemistry

R. W. Braun, A. H. Cowley,\* M. C. Cushner, and R. J. Lagow\*

Received \_\_\_\_\_

Trifluoromethylsulfur trifluoride has been prepared by the action of  $F_2$  or oxidative fluorinating agents on  $CS_2$ ,  $CF_3SCl$ , or  $(CF_3S)_2CS$ .<sup>1</sup> However, the commercial availability of  $CF_3SSCF_3$  renders this compound an ideal starting point for the one-step synthesis of  $CF_3SF_3$ . The conversion  $CF_3SSCF_3 \rightarrow 2 CF_3SF_3$  has, in fact, been accomplished previously by treatment with  $CF_3OF$ ,<sup>1c</sup>  $ClF_3$ ,<sup>2</sup> or  $F_2$ .<sup>1c</sup> However, the  $CF_3OF$  and  $ClF_3$  reactions are difficult to control, and the direct fluorination involved a labor intensive batchwise method. The present paper describes a greatly improved procedure for direct fluorination of  $CF_3SSCF_3$  which avoids handling molecular fluorine in Pyrex glass.

Trifluoromethylsulfur trifluoride is generally thought to possess an essentially trigonal bipyramidal geometry in which the  $CF_3$  moiety adopts an equatorial location. However, in view of the controversy which has surrounded the delineation of the ground state geometry of the analogous phosphorane,  $CF_3PF_4$ ,<sup>3</sup> it seemed appropriate to reinvestigate the stereochemical features of  $CF_3SF_3$  by means of  $^{19}F$  dynamical NMR (dnmr) spectroscopy.<sup>4</sup> Furthermore, since erroneous results had been obtained in dnmr studies of  $SF_4$  in Pyrex glass NMR tubes<sup>5</sup> it was decided to employ quartz NMR tubes and an HF scavenger in the present study. Finally, we report the first  $^{13}C$  NMR data for  $CF_3SF_3$ .

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### Experimental Section

The compound  $\text{CF}_3\text{SSCF}_3$  was obtained commercially and purified by fractional vacuum condensation prior to use. The four-zone cold reactor fluorination system has been described previously.<sup>6</sup> A typical reaction involved the injection of 2.0 g of  $\text{CF}_3\text{SSCF}_3$  into the reactor, the second zone of which was maintained at  $-120^\circ$  by means of thermostatically controlled liquid nitrogen cooling. The helium flow was set at 60 ml/min and the fluorine flow at 1 ml/min. Various reaction times were investigated; the optimum time was discovered to be 38 h. Longer reaction times resulted in the production of  $\text{CF}_3\text{SF}_5$ . After 72 h fluorination  $\text{CF}_3\text{SF}_5$  was the only major product. After 38 h the fluorine flow was terminated and the reactor was allowed to assume ambient temperature. The products which had collected in a glass trap were transferred to a standard glass high vacuum line and subjected to fractional distillation with U-traps held at  $-93^\circ$ ,  $-110^\circ$ , and  $-196^\circ$ . The  $-196^\circ$  trap contained  $\text{CF}_3\text{SOF}$  plus traces of  $\text{SF}_6$ ,  $\text{SF}_4$ ,  $\text{CF}_4$ , and  $\text{COF}_2$ . The desired product condensed in the  $-110^\circ$  trap. Based on the  $\text{CF}_3\text{SSCF}_3$  consumed, the conversion to  $\text{CF}_3\text{SF}_3$  was ~90%.

NMR samples were run both with and without  $(\text{C}_6\text{H}_5)_3\text{PNH}$  present as HF scavenger. No spectral differences were discerned throughout the temperature ranges studied. In each experiment the  $\text{CF}_3\text{SF}_3$  had been ~~sample~~ briefly over NaF prior to distillation into the quartz NMR cell. Preliminary  $^{19}\text{F}$  NMR samples were run in 5 mm quartz tubes on a Varian 56/60 instrument. The variable temperature  $^{19}\text{F}$  NMR experiments were conducted on a Varian HA 100 spectrometer. The  $^{13}\text{C}$  NMR measurements were made on 10 mm quartz tubes on a Bruker WH 90

spectrometer operating in the FT mode.

## Results and Discussion

We have found that  $\text{CF}_3\text{SF}_3$  can be prepared in approximately 90% yields by the direct fluorination of  $\text{CF}_3\text{SSCF}_3$  in a continuous flow reactor which features helium dilution and maintenance of the substrate at  $-120^\circ$ . The reaction times were found to be critically important. Optimum yields of  $\text{CF}_3\text{SF}_3$  are produced after a 38 h run; extension of reaction times beyond 38 h generates progressively larger quantities of  $\text{CF}_3\text{SF}_5$ . After 72 h essentially complete conversion to  $\text{CF}_3\text{SF}_5$  occurs.

The  $^{19}\text{F}$  NMR data for  $\text{CF}_3\text{SF}_3$  are displayed in Figure 1, and the F axial ( $F_a$ ) and F equatorial ( $F_e$ ) chemical shift and  $J_{F_a F_e}$  coupling constant data have been assembled in Table I, along with those for analogous  $\text{RSF}_3$  sulfuranes which feature sulfur-carbon bonds, viz. alkyl, perfluoroalkyl,  $\text{C}_6\text{H}_5$  or  $\text{C}_6\text{F}_5$  substituents.

Two trigonal bipyramidal models can be considered for  $\text{RSF}_3$  molecules,



It is clear that both the axially substituted model, 1, and the equatorially substituted model, 2, will yield  $\text{AX}_2$  (or  $\text{AB}_2$ )  $^{19}\text{F}$

NMR spectral patterns under the condition of slow ligand permutation. The differentiation of the structures must, consequently, rely on  $^{19}\text{F}$  chemical shift data. The  $F_a$  and  $F_e$  chemical shift assignments in Table I exhibit a very consistent pattern. The premise upon which these assignments are based is that  $\text{CH}_3\text{SF}_3$  must adopt structure 2 because of the very small apicophilicity of the  $\text{CH}_3$  group.<sup>7</sup> It may, therefore, be concluded that  $\text{CF}_3\text{SF}_3$ , like the other C-S bonded compounds prefers structure 2.

The  $^{19}\text{F}$  NMR spectra of  $\text{CF}_3\text{SF}_3$  are unchanged up to  $75^\circ\text{C}$ , thus implying a barrier to intramolecular fluorine exchange in excess of 17 kcal/mole. The conformational stability of  $\text{CF}_3\text{SF}_3$  is remarkable in view of the fact that fluorine exchange in the phosphorane analogs,  $\text{CF}_3\text{PF}_4$  and  $(\text{CF}_3)_2\text{PF}_3$ , persists down to  $-150^\circ$ .<sup>3</sup>

The ambient temperature  $^{13}\text{C}$  NMR spectrum of  $\text{CF}_3\text{SF}_3$  consists of the anticipated 24 line spectrum centered at 122 ppm relative to external  $(\text{CH}_3)_4\text{Si}$  (Figure 2) with  $J_{\text{CF}} = 323.6$ ,  $J_{F_a\text{SC}} = 11.8$ , and  $J_{F_e\text{SC}} = 19.1$  Hz. These data confirm the stereochemical rigidity of  $\text{CF}_3\text{SF}_3$  at ambient temperature. The fact that  $J_{F_e\text{SC}}$  is slightly larger than  $J_{F_a\text{SC}}$  may be a reflection of the fact that the equatorial plane of a trigonal bipyramid features more sulfur 3s character than the axes. The differences in the axial and equatorial F-S-C couplings may be useful for the stereochemical assay of fluorosulfuranes.

Acknowledgment. The authors are grateful to the Office of Naval Research (Contract N00014-76-C-0577, Task No. NR 053-612) for financial support. Gratitude is also expressed to the Jet Propulsion Laboratory, Pasadena, California for the loan of the Varian A 56/60 NMR spectrometer.

Table I. Nmr Data for  $\text{CF}_3\text{SF}_3$  and Related Compounds<sup>a</sup>

<u>Compound</u>	<u>F<sub>a</sub></u>	<u>F<sub>e</sub></u>	<u>J<sub>F<sub>a</sub>SF<sub>e</sub></sub> (Hz)</u>	<u>Reference</u>
$\text{CF}_3\text{SF}_3$	-52	+48	67	b
$\text{CH}_3\text{SF}_3$	-60	+51	72	c
$(\text{CF}_3)_2\text{CFSF}_3$	-61	+54	4.8	d
$\text{C}_6\text{H}_5\text{SF}_3$	-72	+26	53	e
$\text{C}_6\text{F}_5\text{SF}_3$	-73	+50	70	f

<sup>a</sup>  $^{19}\text{F}$  chemical shifts in ppm relative to  $\text{CCl}_3\text{F}$ . Upfield shifts from  $\text{CCl}_3\text{F}$  are considered to be positive.

<sup>b</sup> This work. These data are in essential agreement with earlier work.

<sup>c</sup> Reference 4b

<sup>d</sup> R. M. Rosenberg and E. L. Muetterties, Inorg. Chem., 1, 756 (1962).

<sup>e</sup> Reference 1b

<sup>f</sup> P. Meakin, D. W. Ovenall, W. A. Sheppard, and J. P. Jesson, J. Am. Chem. Soc., 97, 522 (1975).

## References and Notes

- (1) (a) E. A. Tyczkowski and L. A. Bigelow, J. Am. Chem. Soc., **75**, 3523 (1953); (b) W. A. Sheppard, ibid., **84**, 3058 (1962); (c) C. T. Ratcliffe and J. M. Shreeve, ibid., **90**, 5403 (1968).
- (2) G. H. Sprenger and A. H. Cowley, J. Fluorine Chem., **7**, 333 (1976).
- (3) For a summary of this controversy, see R. C. Cavell, J. A. Gibson, and K. I. The, J. Am. Chem. Soc., **99**, 7841 (1977).
- (4) For previous  $^{19}\text{F}$  nmr data on  $\text{CF}_3\text{SF}_3$  at ambient temperature or below, see (a) reference 1c and (b) W. Gombler and R. Budenz, J. Fluorine Chem., **7**, 115 (1976), and references therein.
- (5) W. G. Klemperer, J. K. Krieger, M. D. McCreary, E. L. Muetterties, D. D. Traficante, and G. M. Whitesides, J. Am. Chem. Soc., **97**, 7023 (1975), and references therein.
- (6) N. J. Maraschin, B. D. Catsikis, L. H. Davis, G. Jarvinen, and R. J. Lagow, J. Am. Chem. Soc., **97**, 513 (1975).
- (7) For phosphoranes the order of apicophilicity is (in part)  $\text{F} > \text{Cl} > \text{Br} > \text{CF}_3 > \text{alkyl}$ . See reference 3.

Figure Captions

Figure 1. 94.1 MHz  $^{19}\text{F}$  nmr spectra of  $\text{CF}_3\text{SF}_3$  at 29° C (a) axial ( $\text{F}_a$ ) region, (b) equatorial ( $\text{F}_e$ ) region, and (c)  $\text{CF}_3$  region (+ 69.9 ppm relative to internal  $\text{CCl}_3\text{F}$ )

Figure 2. 22.6 MHz  $^{13}\text{C}$  nmr spectrum of  $\text{CF}_3\text{SF}_3$  at 30°C.

Fig. 1

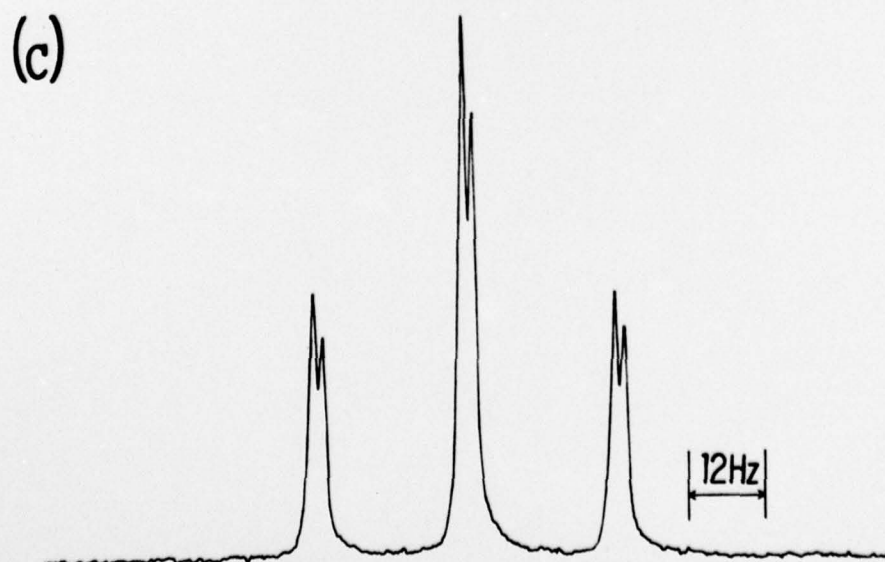
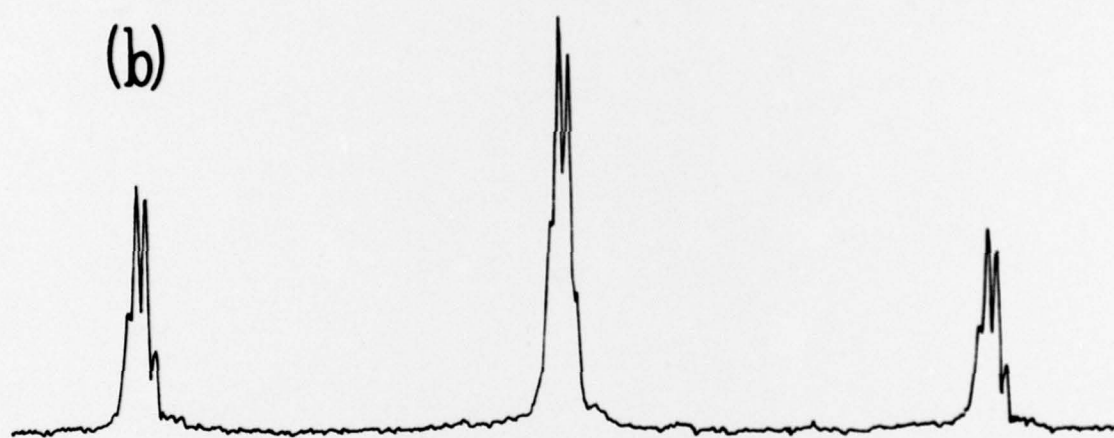
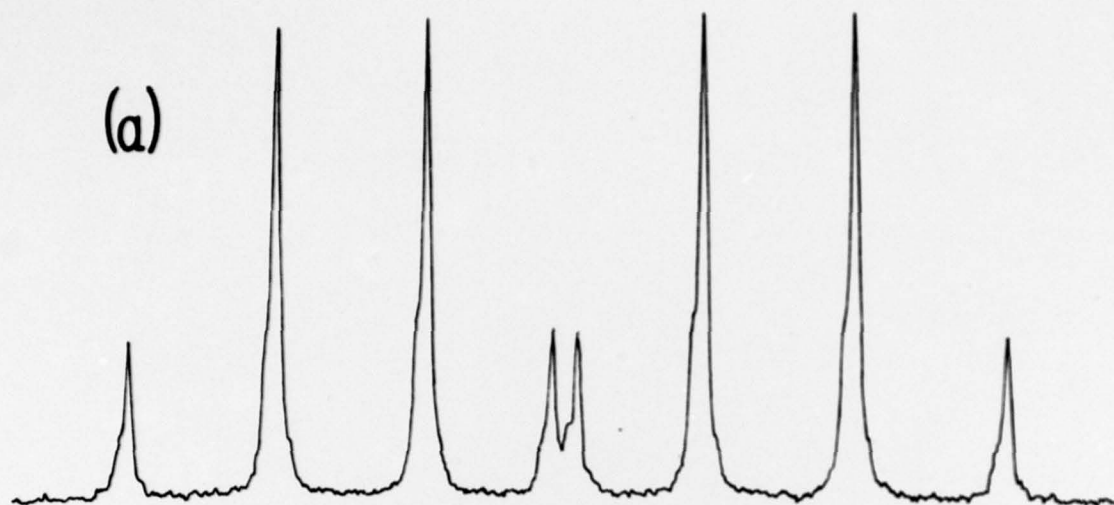


Fig. 2

